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Description

The invention relates to compositions comprising effective amounts of a salt of a monoester of citric acid as skin-smoothing or softening agents. Additionally, an improved method of synthesizing monoesters of citric acid is claimed.

BACKGROUND OF THE INVENTION

Many compositions used for treating human skin impart unpleasant feel to the skin during or after use. Thus, many compositions containing soap, detergent or both and intended for cleansing the skin may dry the skin and leave it feeling rough, chapped and flaky. The drying effect of these compositions (which include toilet bars, liquid or powder hand washing and bubble bath compositions may be extremely pronounced in certain seasons, as in dry winter months. Use of such washing compositions during these seasons may dry the skin to the point of scaliness or brittleness, with resultant cracking, reddening, bleeding and soreness.

Other products applied to the skin such as shaving creams, foams or oils may also have a drying effect on skin. Moreover, the skin is stretched, scraped and often cut or punctured during shaving. These operations accompanying use of these products may exacerbate skin drying and increase skin feeling of roughness, flakiness and brittleness.

Products for the treatment of skin dryness include oils, balms, creams, lotions, liniments, ointments, unguents and gels. While these products may moisten skin and reduce or reverse roughness, cracking and brittleness of dry skin, many such products leave an unpleasant residue causing the skin to feel sticky, stiff, inflexible and waxy or unduly oily and greasy. Other products which may leave an unpleasant residue on the skin or which could benefit by improvement in skin treatment qualities include insect repellent and bite compositions, antiseptics and skin burn compositions (for burns from heat, sun or wind). Additionally, compositions for chapped lips such as lip balm or cream may impart an unpleasantly waxy or greasy feeling to the lips.

Citric acid derivatives have been incorporated in a wide variety of compositions. A salt of a monoester of citric acid, made from citric acid and alkanols of 1-18 or alkenols with up to 10 carbon atoms, is used to stabilize vinyl halide polymers in U.S. Patent No. 3,362,923 (Kruth). Non-salt alkyl esters of citric acid in U.S. Patent No. 3,929,712 (Hiyama et al.) are said to impart lubricant properties to vinyl chloride resins, each alkyl group having 12-22 carbons. Non-salt monoesters of citric acid are said to deactivate metals in petroleum products, e.g. cracked gasolines, according to U.S. Patent No. 2,747,979 (Thompson). The radials which esterify the citric acid may be alkyl or benzyl.

Monoesters of citric acid have also been used in treating clothes, as in U.S. Patent No. 3,754,860 (Frick, Jr. et al.) where citrate monoesters with a small or moderate size aliphatic chain (up to 2-ethylhexyl) are included in wrinkle-resistant fabric finishes, and U.S. Patent No. 3,971,626 (Heyden et al.) where a citric acid ester with a fatty alcohol of 12-22 carbon atoms is incorporated in a leather-treating agent. Particularly disclosed in Hayden et al. are citric acid esters with straight-chain unsaturated fatty alcohols and branched saturated or unsaturated fatty alcohols.

Monoesters of citric acid are also employed in the food technology art. U.S. Patent No. 2,158,678 (Gooding et al.) describes agents said to retard the development of rancidity and improve moisture retention in glyceridic oil compositions, e.g., margarine. These agents, defined at col. 1, line 45 to col. 2, line 25, include monolauryl citrate and monostearyl citrate. Related U.S. Patent No. 2,523,792 (Vahlteich et al.) describes edible compositions which are said to retard rancidity in glyceridic oils and which have 15 to 37.5% of selected monoesters of citric acid (including monolauryl, monomyristyl, monopalmityl, monooleyl and monostearyl citrate) dissolved in a solubilizing agent, e.g. lecithin. Monoesters of citric acid are also said to retard deterioration of milk and egg products in U.S. Patent 2,667,419 (Gooding et al.). Citric acid monoesters of decanols, dodecanols, hexadecanols, and octadecanols are particularly disclosed and more particularly monolauryl and monostearyl citrate. Also, U.S. Patent No. 2,902,372 (Harris) discloses monoesters of citric acid with aliphatic alcohols of less than 3 carbon atoms for the purpose of improving the whipping properties of egg whites. Finally, U.S. Patent No. 3,004,853 (Julian et al.) discloses citric acid esterified with cetyl alcohol as part of an emulsifier system in a liquid shortening.

Other emulsifiers derived from citric acid, useful in the foods industry or cosmetology, are disclosed in U.S. Patent No. 3,929,870 (David et al.). Specific citric acid derivatives in cosmetics include certain triesters of citric acid for shampoos disclosed in U.S. Patent No. 4,176,176 (Cella) and 1-25% of citric or acetylcitric acid esterified by aliphatic alcohols having 1-6 carbon atoms for deodorant sticks and sprays disclosed in U.S. Patent No. 4.010,253 (Reese et al.). European Patent 8105 (BASF) describes cosmetic preparations

having 4-40% of citric acid esters carrying branched-chain alcohol radicals having 8-13 carbon atoms such as Tris-isodecyl citrate. German Patent No. 2,361,716 (Henkel) describes cosmetic preparations having 0.5-15% of coesters made from a) aliphatic diols, b) citric or acetylcitric acid, and c) aliphatic monofunctional alcohols having 12-30 carbon atoms. Preparations incorporating the coester are said to be soft and to produce no unpleasant feeling of sticking to the skin.

Citric acid or its derivatives have also been incorporated in toilet bars. Romanian Patent No. 72,330 (Grigorescu) describes incorporating citric acid in a cosmetic soap. U.S. Patent No. 4,292,192 (Hooper) states that incorporating 0.3 to 3% of citric or acetylcitric acid esterified by an alkyl group of 1 to 4 carbon atoms imparts a deodorancy property to personal washing bars. (Another monoester incorporated in a personal washing composition, although not a citric acid derivative, is $ROOC-(CH_2)_n-COOM$, where R is an alkyl or alkenyl chain with 4-12 carbon atoms, n = 2-4 and M is a cation disclosed in the currently pending U.S. Patent application of Nambudiry et al., Serial No. 914,022, filed October 1, 1986 for Detergent Compositions.)

Citric acid derivatives have also appeared in detergent compositions as pollution control substitutes for other components. Thus, U.S. Patent No. 3,816,318 (Hentschel) discloses washing, dishwashing and cleaning detergent compositions which include 5 to 30% of salts of certain monoesters derived from polybasic carboxylic acids and alcohols of at least 1 hydroxyl group and 1-8 carbon atoms. Hentschel states that owing to strengthened lipophilicity, the monoesters have heightened emulsifying properties. Specific monoester salts are disclosed.

U.S. Patent No. 4,271,032 (Kolaian et al.) discloses compositions for removing soil from fabrics in laundering. The compositions include monoesters of certain polycarboxylic acids, the alcohol radical having 12-30 carbon atoms. The monoesters are said to be effective as a surfactant or as a builder. European Patent No. 199,131 (Raffineria Olii Lubrificanti), published October 29, 1986, describes surfactants derived from citric acid, namely citric acid mono-, di- and triesters with alkoxylated alcohols described therein. Mixtures of these esters are said to be very efficient surfactants with excellent detergent and biodegradability properties and with little or no toxicity or skin irritancy. Mixtures of the esters are also said to be suitable for a liquid detergent for kitchenware as well as liquid or creamy skin detergents or bath foam, as set out in the Examples.

It has been discovered that salts of certain monoesters of citric acid impart desirable qualities to skin treatment compositions.

Some conventional methods of synthesizing monoesters of citric acid yield a mix of mono-, di-, and triesters of citric acid. The mixed mono-, di- and triester products of these methods is impractical in many applications. Only the monoester is soluble in alkaline aqueous systems. Additionally, the di-, and triesters severely limit foaming. Thus, it would be desirable to produce monoesters of citric acid in a pure form, or in such predominance that the problems due to di- and triesters would be insignificant.

In the first of these methods, citric acid is reacted directly with an alcohol: the blend is heated, agitated until a solid forms, and cooled under reduced pressure, as described in U.S. Patent Nos. 2,523,792 (Vahlteich) and 3,929,870 (David et al.).

A second method involves mixing citric acid in a dioxane solvent and adding an alcohol. The reaction mixture is refluxed for up to 72 hours, then the dioxane evaporated under reduced pressure. The remaining residue is diluted, then is stripped at 60 °C under reduced pressure. This method is described in U.S. Patent No. 4,271,032 (Kolaian et al.). The yield of monoester of citric acid from both these direct esterification methods is about 60%. It is noted that dioxane is not only an expensive solvent; its use may be accompanied by peroxide compounds which, upon accumulation, may be explosive.

While the methods of synthesizing monoesters of citric acid produce a mixture of mono-, di- and triesters, the relative molar amounts of citric acid and alcohol affect whether the mono,- di- or triester product predominates. Thus, reacting substantially equal molar amounts of citric acid and alcohol (or a greater amount of the former) favors monoester, while diester predominates when a molar amount of alcohol double that of citric acid is used.

One process which exploits this effect is described in U.S. Patent No. 2,518,678. Citric acid is dissolved in dry pyridine. Stearyl alcohol is added to the solution and heated for 20 hours. Since only a small concentration of stearyl alcohol is said to be soluble in the pyridine solution, a small concentration of the alcohol is continually reacted with a large concentration of citric acid, favoring monoester formation.

However, even this process produces a mixture of mono-, di- and triesters, requiring expensive and cumbersome steps to purify the monoester such as the techniques of fractional crystallization and selective extraction with suitable solvent systems described in U.S. Patent Nos. 2,518,678 and 2,523,792.

A. J. Repta et al. "Synthesis, Isolation , and Some Chemistry of Citric Acid Anydride", Journal of Pharmaceutical Sciences 58, (September 1969), pages 1110-1114, describes synthesis of citric acid

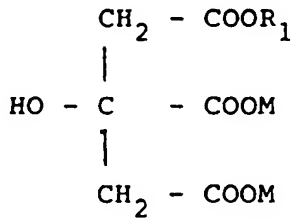
anhydride at page 1, col. 2, lines 14-31 and page 2. Suggested uses of the anhydride are as a dessicant or an ingredient in formulations for carbonation.

In the Nambudiry application cited above, monoesters are prepared by mixing and heating an acid anhydride, e.g. succinic anhydride, with fatty alcohol.

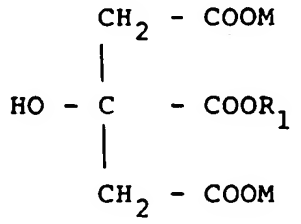
It has been discovered that monoesters of citric acid may be produced with minimal levels of di- and triester if citric acid is first reacted to form citric acid anhydride then reacted to form the monoester.

SUMMARY OF THE INVENTION

This invention provides a skin treatment composition comprising from 1% to 35% by weight of dication salt of one or a mixture of monoesters of citric acid having either of the following formulae:



(I)



(II)

where R_1 has the structure of a moiety derived from R_1-OH, which alcohol is chosen from alkanols, alkenols and arylalkanols having from 10 to 18 carbon atoms;
each M is a cation independently chosen from alkali metals, the alkaline earth metals, ammonium, mono-, di- and trialkanol ammonium; and
a physiologically acceptable carrier for said monoester.

It has been discovered that such a composition has the desirable quality of imparting to skin a marked smooth and creamy feel. It has further been discovered that toilet bars incorporating a salt of a monoester of citric acid themselves have an unusually pleasant smoothness and slip.

Skin treatment compositions incorporating 1-35% of a dication salt of a monoester(s) of citric acid in accordance with this invention may be toilet bars, liquid hand washing compositions, shaving cream, antiseptics, insect repellent or bite compositions, and skin treatment compositions, for dry, rough or chapped skin or skin burned by heat, sun or wind.

The skin treatment composition of the instant invention may be in the form of a cream, liniment, oil, balm, ointment, solution, gel or unguent and may be applied directly to the skin. Incorporation of such compositions in pads, plasters, bandages, dressings, and pre-moistened towelettes, all optionally carrying medication in addition to the skin treatment composition, results in products embraced by this invention.

Without in any way limiting the scope of the present invention to the following theorectical considerations, applicant would like to emphasize his belief that it is the salt of the monoester of citric acid (rather than any di- or triester which may be present at very low levels) which contributes to the smoothening effect of the skin, and that maximizing the level of the monoester salt in skin treatment compositions results in markedly improved products. Moreover, it is important that the R_1 chain of the monoester be long enough to impart adequate hydrophobicity to the composition and to produce the smoothness and slip of such compositions. Consequently, it is monoesters having higher R_1 chain lengths which are included in the skin treatment compositions of the invention. These R_1 chains are typically straight chains, i.e., unbranched and not alkyl substituted.

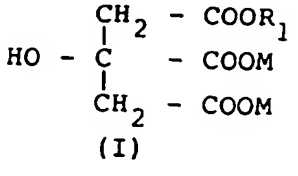
Pure or predominantly monoester is desirable for reasons stated above. It has been discovered that monoesters of citric acid may be synthesized with minimal production of di- or triesters: about 95% of the esterified citric acid is in monoester form, the balance being an acetyl derivative of the monoester. This new process produces higher yields in less time (75% and above in less than 12 hours) of a nearly pure monoester, and avoids the expense and difficulties associated with the solvent dioxane and purification of the monoester from the di- and triesters.

The process comprises heating citric acid with an organic anhydride to form citric acid anhydride. Then an alcohol of the formula R_1-OH is added to the reaction mixture, R_1-OH being defined as above. The

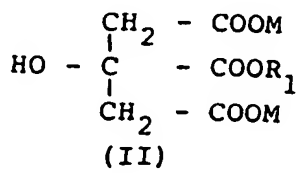
reaction mixture is then continually distilled under reduced pressure to remove volatile materials such as liberated short chain acid side products. The monoester product may then be isolated as a dication salt and, if desired, isomers I and II may be purified. The isomer of formula (II) predominates in the product of this method by about a factor of 3, while the isomer of formula (I) predominates in the product of direct esterification by about a factor of 3.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to skin-smoothing compositions, which comprise, in admixture with a pharmaceutically acceptable carrier vehicle, an effective amount of a salt of a monoester of citric acid having one or both of the following formulae:



(I)



(II)

where R_1 is derived from R_1-OH, which alcohol is chosen from alkanols, alkenols, and arylalkanols having 10 to 18 carbon atoms; and

where M is a cation independently chosen from alkali metals, alkaline earth metals, ammonium and mono-, di-, and trialkanol ammonium.

Compositions of this invention include a salt of an ester of citric acid. This ester of citric acid may consist essentially of the monoester of citric acid or may comprise of mixture of mono-, di- and triesters of citric acid.

The compounds of formulae (I) and (II) are isomeric forms of a salt of a monoester of citric acid, (II) being a symmetrical and (I) an asymmetrical isomer. Compositions of the present invention may have either isomer or a mixture of both.

In a preferred embodiment, which both isomers are present, the relative amount of (II) to (I) may be about 3:1. Additionally, the monoester salts of citric acid need not all have identical R_1 groups. Furthermore, each molecule of the salt of a monoester of citric acid may have two of the same or different cations; if all the salt molecules have the same cations, the cations need not be the same from molecule to molecule.

R_1 may more particularly have the structure of a moiety derived from R_1-OH, which alcohol is chosen from straight chain alkanols and alkenols having 10 to 18 carbon atoms; or chosen from alkanols and alkenols having 12 to 15 carbon atoms. One commercially available mixture of alkanols which is suitable for esterifying citric acid has primary alcohols with 14 to 15 carbon atoms, sold as NEODOL® 45. The NEODOL® products are available ex Shell Oil Company, One Shell Plaza, Houston, TX 770022.

Instead of the 1 to 35% of a salt of a monoester of citric acid the composition of the inventions may more particularly include from 5 to 30% or from 10 to 25% of the salt of a monoester of citric acid. At levels over 35%, compositions which are intended to be solid may become soft, mushy and pliable. (All component amounts expressed in percentages indicate percent weight unless otherwise stated.)

The compounds of formulae I and II may be incorporated in a physiologically acceptable carrier of petroleum jelly, lanolin, paraffin wax, alkanols, water and mixtures thereof as well as the carriers of the examples below. More particularly, the water may be a 1-5% solution of an appropriate buffer, such as sodium bicarbonate. The physiologically acceptable carrier may comprise soap or detergent toilet bars, or liquid or powder hand washing compositions, antiseptics, insect repellent and bite compositions, shaving creams, oils and foams, and compositions for treatment of dry, rough or chapped skin. Some formulations of the composition may be applied briefly and washed off as in washing hands with a toilet bar within the invention, while other formulations such as a cream or ointment described below, may be left on indefinitely.

The skin treatment composition of the present invention may take any of the following forms: lotion, liniment, solution, suspensions, oil, ointment, cream, gel, balm, unguent, paste, stick or aerosol and may be applied directly to the skin. Application may also take place in using one of the consumer products listed above, e.g. in washing hands with a toilet soap bar. Alternatively, the skin treatment composition of this invention may be incorporated in pads or pre-moistened towelettes for a wiping application to the skin or onto bandages, dressings or plasters for a longer application. The bandages, dressings, pads, plasters and

pre-moistened towelettes may be optionally medicated with substances in addition to the skin treatment composition.

Conventional soap compositions typically are comprised of from 25 to 90% by weight of soap from 1 to 15% water. When such compositions further incorporate salt of monoester of citric acid within one of the above-recited ranges, the compositions come within the present invention. The term "soap" is used herein to mean the alkali metal or alkanol ammonium salts of aliphatic alkane- or alkene- monocarboxylic acids having about 12 to about 20 carbon atoms, and preferably about 12 to 18 carbon atoms.

It is preferred to use soaps having the fatty acid derived from coconut oil, tallow, or mixtures thereof, since these are among the most readily available fats. The proportion of fatty acids having at least 12 carbon atoms in coconut oil soap is about 85%. This proportion will be greater when mixtures of fatty acids derived from fats such as tallow, palm oil, or non-tropical nut oils or fats are used, wherein the principal chain lengths are of sixteen carbon atoms or more. The tropical nut oils include: palm kernel oil, babassu oil, ouricuri oil, tucum oil, cohune nut oil, murumuru oil, jaboty kernel oil, khakan kernel oil, dika nut oil, and ucuhuba butter. A preferred soap for use in the compositions of this invention has at least about 85% fatty acids having 12-18 carbon atoms.

Derivation of fatty acids from oils and fats for use in this invention is by known methods, e.g. saponification of said oil or fat.

An especially preferred soap composition comprises a mixture of alkali metal salts of fatty acids of which 10 to 70% are derived from coconut, and 90 to 30% are derived from tallow. More particularly, 15 to 20% of the fatty acids may be derived from coconut oil and 75 to 85% from tallow. These mixtures contain about 95% fatty acids having 12 to 18 carbon atoms.

Additionally, optional ingredients may be included in soap formulations of the present invention, e.g., free fatty acids, emollients, suds boosting agents, germicides, opacifiers (such as titanium dixoide) and colorants, pigments, perfumes, preservatives, electrolyte salts and mixtures thereof. A typical listing of the classes and species of optional ingredients useful in soap compositions appears in U.S. Patent 4,260,507 incorporated herein by reference. It should be understood, of course, that these lists of optional ingredients and mixtures for soap compositions are only representative of such materials and is not intended to be limiting.

The soap compositions of the present invention may be in liquid or solid form. The latter form is well known commercially as the toilet bar. Requirements for a good toilet bar are well known and enumerated in U.S. Patent 2,894,912. The properties of soap toilet bars of the present invention are similar to those of conventional bars with the addition of properties herein disclosed.

Soaps and Detergents, Thomssen and McCutcheon, MacNair-Dorland Company, 1949, pp. 195-207 and Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, 1983, Vol. 4, pp. 173-177 describe techniques of toilet bar-making including milling, plodding, framing and shaping, by means of which the soap compositions of this invention may be shaped into bars. A bar of toilet soap may be formed by these techniques from the following composition: about 80% of fatty acids derived from tallow and coconut, about 10% water and about 10% of disodium salt of a monoester of citric acid esterified with C_{12}-C_{15} (3 EO) primary alcohols. The bar itself has a remarkable smoothness and slip; washing with one's skin with the bar imparts a pleasant smoothness to the washed skin.

Non-soap skin-cleansing compositions may also come within this invention. These skin-washing compositions, with detergent active compounds replacing all or part of the soap in the toilet soap bars, are comprised of from about 10% to about 70% by weight of a detergent active compound, about 2% to about 20% suds booster, about 10% to about 40% by weight aliphatic fatty acid, about 2.5% to about 25% by weight water-soluble aliphatic fatty acid soap, about 1% to about 35% by weight of a salt or salts of monoester of citric acid and about 1% to about 10% by weight water. Additionally, the optional ingredients which may be included in these compositions are the same as those listed above for soaps.

Examples of detergent active compounds usable to form these compositions are found in "Surface Active Agents" by Schwartz & Perry (Interscience 1949) and "Surface Active Agents" by Schwartz, Perry & Berch (Interscience 1958) and those set forth in U.S. Patent 2,894,912 and U.S. Patent 3,070,547, each of which is hereby incorporated by reference. More particularly, the detergent active may be selected from the group consisting of alkali metal, magnesium or ammonium salts of detergents selected from the group consisting of C_{12}-C_{16} hydroxyalkane sulfonates, C_8-C_{18} N-acyl taurates, C_{12}-C_{18} alkyl sulfates, C_{12}-C_{18} alkyl ether sulfates, C_{12}-C_{16} alkyl phosphonates and phosphates, C_{12}-C_{16} mono-alkyl succinates and maleates, C_6-C_{14} dialkylsulfosuccinates, C_{15}-C_{20} alkane disulfonates, C_8-C_{18} alkene sulfonates, alkylbenzene sulfonates and mixtures thereof. Further, the detergent active may be an alkali metal, magnesium or ammonium salt of a fatty acyl ester of isethionic acid, in particular fatty acyl esters derived from fatty acids having from 10 to 18 carbon atoms; more particularly the fatty acyl groups may be derived from fatty acids

derived from coconut oil.

These skin cleansing compositions may be liquid or solid. The solid compositions may be formed into toilet bars according to the steps set forth in Thomssen and McCutcheon for soap bars. The properties of the detergent toilet bars of the present invention are similar to those of soap bars as well as to those of conventional bars with the addition of properties herein disclosed.

Skin-cleansing compositions of the present invention may incorporate soap or detergent active compounds or both. In addition to 10-35% of one of the soaps or detergent active compounds discussed above, or a mixture of both, a liquid hand cleansing composition of the present invention comprises 1 to 35% of a salt of a monoester of citric acid, 0-5% sodium chloride, and balance water. Optionally, this composition may further include 1-5% of a suds boosting agent, for example, coco monoethanolamide and 0.2-0.5% of a preservative, for example, EDTA.

When the composition of this invention is a toilet bar or liquid hand cleansing composition, it is desirable that little or no triester or salt of diester of citric acid be present, as these have been found to limit foaming and are insoluble in alkaline aqueous systems.

Shaving creams within the present invention comprise 1 to 35% of a salt of a monoester of citric acid, 25-50% stearic acid, 5-20% coconut oil, 10-25% glycerol, 1-15% mineral oil and 5-45% water.

A composition for treating dry, rough or chapped skin such as chapped lips under the present invention may be in solid form for use as a stick-type composition. Such compositions comprise from 1 to 35% of a salt of a monoester of citric acid, and from 50% to 98%, preferably 60% to 90%, of an emollient. This composition may further comprise from 1% to 20%, preferably 5% to 15%, of a suitable thickening agent, and optionally emulsifiers and water.

A typical listing of suitable thickening agents, emollients and emulsifiers useful in solid compositions appears in U.S. Patent No. 4,560,549 (Ritchey et al.) incorporated herein by reference. It should be understood, of course, that the list of optional ingredients and mixtures there described is representative only and is not intended to be limiting. Additives commonly found in topical compositions such as preservatives, e.g. methyl and ethyl paraben, dyes and perfumes are advantageously included in any of the above-described solid compositions for treating dry, rough or chapped lips.

Compositions for treating dry, rough or chapped skin further may be in ointment form comprising 1 to 35% of a salt of a monoester of citric acid, 1 to 5% anhydrous wool fat, 5 to 20% viscous paraffin, 0 to 5% cetyl alcohol and 65-95% white petroleum jelly. More particularly, the cetyl alcohol may be present at 0.5-2.5%.

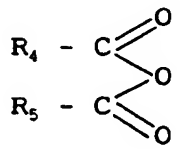
When the skin treatment composition of the present invention is in cream form, it comprises 1 to 35% of a salt of a monoester of citric acid, from 50 to 5%, preferably 25 to 10% of an emollient, and the balance water. Optionally, the cream form contains a suitable emulsifier. The emollients and emulsifiers described above for compositions of the invention in stick form are equally suitable here.

The compositions of this invention may also be formulated in solution form, comprising from 1 to 35% of a salt of a monoester of citric acid, and 65 to 99% of a suitable organic solvent. Suitable organic materials useful as the solvent or a part of a solvent system are as follows: propylene glycol, glycerine, ethanol, sorbitol esters, 1,2,6-hexanetriol, isopropanol, diethyl tartrate, butanediol, and mixtures thereof. Such solvent systems can also contain water.

The compositions of this invention may also be formulated in aerosol form by incorporating the solution formulation described above in a closed metal container fitted with an aerosol cap and pressurized using conventional methods at from 25 psi up to 100 psi pressure with an aerosol propellant such as butane gas.

In a gel form, the present invention comprises 1 to 35% of a salt of a monoester of citric acid, 5 to 75% and preferably 10-50% of an organic solvent, 0.5 to 20%, preferably 1 to 10% of a thickening agent, the balance being water. Suitable thickening agents include those recited above for compositions in solid form. Suitable organic solvents include but are not limited to glycerine, sorbitol esters, 1,2,6-hexanetriol, ethanol, isopropanol, diethyl tartrate, butanediol, and mixtures thereof.

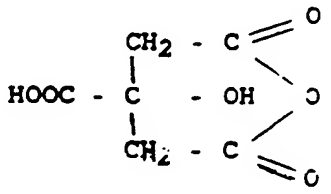
Synthesis of monoesters of citric acid may be carried out by mixing citric acid with an organic anhydride of the formula (V):



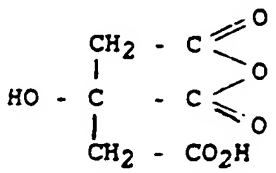
(V)

where R_4 and R_5 are independently selected from the group consisting of hydrocarbon chains having from 1 to 5 carbon atoms or, with R_4 and R_5 taken together, containing 6 to 8 carbon atoms linked to form a cycloaliphatic or aromatic anhydride or substituted derivative thereof. More particularly, the anhydride may be acetic anhydride. The amount in moles of anhydride added is substantially equal to or slightly greater than the amount in moles of citric acid.

In a preferred process, the citric acid and anhydride reaction mixture is heated to a temperature of from 60°C to 90°C for 15 to 45 minutes, producing citric acid anhydride, which is believed to have one of the following formulae:



(VI)



(VII)

Regardless of the structure of any product or any intermediate in the reaction mixture at this stage, an alcohol of the formula R_1-OH may be added directly to the reaction mixture, R_1-OH being selected from the group previously defined. The amount in moles of alcohol added is substantially equal to or slightly less than the amount in moles of citric acid used to form the initial reaction mixture.

The citric acid anhydride and alcohol are subjected to heat and continuous distillation under reduced pressure to remove volatiles and produce predominantly the monoester of citric acid. In a preferred embodiment, the reaction mixture is heated to 60°-80°C and continuously distilled at reduced pressure for 5-10 hours.

The monoester is in solution at this point. To isolate the monoester as a dication salt, the solution is cooled, diluted and neutralised with an organic or inorganic base. For example, the solution may be cooled to room temperature (25°C) or below, diluted with a solvent such as ethanol or methanol, then neutralized to a pH of about 6.0 to about 8.5 with the solution at 15°C or below. Organic or inorganic bases such as sodium hydroxide potassium hydroxide, ammonia solutions, ammonium or substituted ammonium (particularly monoethanolamines), or salts thereof, alkali metal carbonates or alkaline earth metal carbonates or bicarbonates, or mixtures thereof may be used to neutralize the solution. The choice of the neutralizing reagent is governed by which salt or salts of the monoester of citric acid one wishes to form since the cation of the neutralizing reagent becomes the cation of the monoester salt. The solid precipitate which forms is the salt of a monoester of citric acid of formula (1) or (II) above.

Alternatively, in another reaction mode, the citric acid may initially be placed in a solvent, such as acetone or an acid of the formula R_6-COOH, where R_6 is selected from the group consisting of hydrocarbon atoms having from 1 to 5 carbon atoms. An amount in moles of organic anhydride of the above formula (V) substantially equal to or slightly greater than the amount in moles of citric acid is added to the solution. The remainder of the steps are similar to those above.

Preferably, the citric acid used to form the monoester is anhydrous, to prevent lower yields due to hydrolysis of the anhydride reagent by water which may otherwise be present. Solvents employed for the citric acid preferably are also anhydrous.

It is an advantage of this process that predominantly monoesters are produced, i.e. about 95% of the esterified citric acid, the balance being an acetyl derivative of the monoester and minimal levels of di- and or triesters of citric acid. The synthesis thus produces nearly pure monoester of citric acid.

Like the conventional direct esterification methods, the instant synthetic method yields a mixture of symmetrical and unsymmetrical isomers of citric acid monoester. However, the two methods yield relatively different isomeric products: the anhydride synthesis yields mainly symmetrical isomer predominating by about a factor of three over the unsymmetrical ester, while direct esterification yields mainly unsymmetrical ester predominating by roughly the same factor.

These isomers may be isolated from one another by known methods, among which are re-crystallization techniques. A preferred approach for isolating the symmetrical isomer of citric acid monoester from the unsymmetrical isomer follows: the monoester may be dissolved in a solvent system comprising 9 parts heptane and two parts ethyl ether. Adding an additional 1.5 parts ethyl ether induces precipitation. Once precipitation is complete, the solution may be filtered yielding pure symmetrical ester with melting point of

78-80.5 • C.

In addition to the two isomeric forms of the monoester of citric acid, the citric acid anhydride process may form small amounts of diesters. However, the second ester linkage of this diester forms at the hydroxyl group of citric acid rather than at one of the carboxyl groups. The diesters apparently result from the reaction of the citric acid hydroxyl group with the short chain organic anhydride, the acid solvent, when used, or with the acid formed from hydrolysis of the anhydride. Thus, when acetic anhydride reactant for example is used to form citric acid anhydride, there may be formed some acetyl ester of citric anhydride. Subsequent reaction of the latter compound with long chain alcohols, for example, leads to formation of diesters. Such compounds usually comprise far less than 50% of the citric acid monoester product and often comprise less than 10%.

For a further understanding of this invention, reference may be made to the following examples:

EXAMPLE I

A cream is prepared by mixing the following ingredients together:

Disodium mono-n-tetradecylcitrate	20%
Ethoxylated cholesterol	20%
Sorbitol	5%
Water	balance

The resulting cream is applied to the skin to relieve dryness. Advantageously the cream is applied every four to twelve hours while dryness persists.

EXAMPLE II

A toilet soap bar having the following composition is made by mixing the first three components in a Brabender kneader for 35 minutes at 50 • C then adding the last two components and mixing for 10 minutes more:

Disodium salt of monododecylcitrate	17.6
Mixture of sodium salts of fatty acids, of which 82% are derived from tallow and 18% are derived from coconut oil	76.5%
Water	3.8%
TiO_2	1%
Perfume	1%

EXAMPLE III

A toilet soap bar is made having the following composition by the steps of Example II:

Disodium salt of the monoester of citric acid derived from primary alcohols having 14 to 15 carbon atoms	20%
Mixture of sodium salt of fatty acids of which 82% are derived from tallow and 18% from coconut oil	70%
TiO_2	1%
Perfume	1%
Water	balance

EXAMPLE IV

A detergent toilet bar is made having the following composition: 10% of dipotassium salt of citric acid monoester esterified with primary alcohols having 14 to 15 carbon atoms, 9% water, 50% disodium salt of

lauryl ester of isethionic acid, 10% unesterified sodium salt of isethionic acid, 10% of potassium lauryl sulfate as a suds-boosting detergent salt, and 10% of paraffin wax as a binder-plasticizer. The toilet bar is formed by the conventional steps of toilet bar formation, and imparts a creaminess and smoothness to skin washed with the bar. Additionally, the bar itself has a markedly pleasant smooth hand feel.

EXAMPLE V

A solid stick according to this invention containing a salt of a monoester of citric acid is prepared by shaping and molding the following ingredients:

Disodium mono-n-decylcitrate	20%
Lanolin wax	65%
Glycerol	5%
Methylcellulose	5%
Water	balance

The resultant solid stick of this Example is applied upon the skin to relieve a feeling of dryness, roughness or scaliness.

EXAMPLE VI

An ointment formulation is prepared by thorough mixing of the following ingredients.

Dipotassium salt of a monoester of citric acid esterified with C_{14}-C_{15} primary alcohols	20%
Anhydrous wool fat	2%
Viscous paraffin	10%
White petroleum jelly	balance

The resultant ointment is applied to the skin to relieve a feeling of dryness, roughness or scaliness. Advantageously, the ointment is applied every four to twelve hours while dryness persists.

EXAMPLE VII

A cream is prepared by mixing the following ingredients together.

Disodium mono-n-tetradecylcitrate	20%
Ethoxylated cholesterol	20%
Sorbitol	5%
Water	balance

The resulting cream is applied to the skin to relieve dryness. Advantageously the cream is applied every four to twelve hours while dryness persists.

EXAMPLE VIII

A solution formulation is prepared by mixing the following components at room temperature:

Glycerine	60%
Disodium monolaurylcitrate	15%
Water	balance

The solution is applied to affected skin. Advantageously, the solution is applied every four to twelve hours.

EXAMPLE IX

A gel formulation is prepared by mixing the following ingredients:

Disodium salt of monoester of citric acid esterified with C_{14}-C_{15} primary alcohols	25%
1,2,6-Hexanetriol	45%
Bentonite	8%
Water	balance

EXAMPLE X

Anhydrous citric acid (0.2 moles) and acetic anhydride (0.24 moles) rapidly mixed then heated to 70 • C for 20-30 minutes. Lauryl alcohol (0.18 mole) is added to the reaction mixture, which is then subjected to continuous distillation under reduced pressure at 70-75 • C for 5 hours to remove acetic acid.

The reaction mixture is cooled to 20 • C and diluted with ethanol, then neutralised at 15 • C of pH of 8.5. Sodium carbonate (0.4 moles) is added and the disodium salt of monododecyl citrate is recovered as a precipitate.

EXAMPLE XI

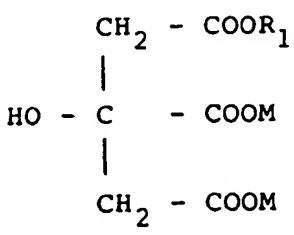
Anhydrous citric acid (0.2 moles) is placed in a vessel and suspended in acetic acid. Acetic acid anhydride (0.24 moles) is rapidly added to the vessel and the mixture is heated to 80 • C for 30 minutes. A mixture of saturated C_{14}-C_{15} aliphatic primary alcohols is added to the vessel. The reaction mixture is continuously distilled at reduced pressure at 70 • C for 10 hours, then cooled to 25 • C.

Ethanol (50 ml) is added to the vessel, then 50% aqueous NaCH is added to neutralise the mixture to about pH 7. The disodium salts of monotetradecyl ester and monopentadecyl ester of citric acid are recovered as precipitate.

In both of Examples X and XI, yields of the disodium salt of monoester of citric acid are from 65% to 80%.

Claims

1. A skin treatment composition comprising from 1% to 35% by weight of dication salt of one or a mixture of monoesters of citric acid having either of the following formulae:



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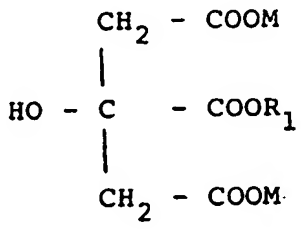


(II)

where R_1 has the structure of a moiety derived from R_1-OH, which alcohol is chosen from alkanols, alkenols and arylalkanols having from 10 to 18 carbon atoms;
each M is a cation independently chosen from alkali metals, the alkaline earth metals, ammonium, mono-, di- and trialkanol ammonium; and
a physiologically acceptable carrier for said monoester.

2. The skin treatment composition according to claim 1, wherein R_1-OH is chosen from straight hydrocarbon chain alkanols and alkenols having from 10 to 18 carbon atoms.

3. The skin treatment composition according to claim 1 or 2, wherein R_1-OH is chosen from alkanols and alkenols having from 12 to 15 carbon atoms.

4. The skin treatment composition according to claim 1, 2 or 3, wherein R_1-OH is lauryl alcohol.

5. The skin treament composition according to any preceding claim, wherein the monoester of citric acid is comprised of symmetrical and unsymmetrical isomers in a relative ratio of about 3:1.

6. The skin treatment composition according to any preceding claim, comprising from 5% to 30% by weight of salt of one or a mixture of monoesters of citric acid of formulae (I) or (II), from 25% to 90% by weight of soap, and the balance water.

7. The skin treatment composition according to claim 6, wherein fatty acids of the soap are derived from tallow.

8. The skin treatment composition according to claim 6, wherein fatty acids of the soap are derived from a vegetable oil.

9. The skin treatment composition according to claim 8, wherein the vegetable oil is coconut oil.

10. The skin treatment composition according to claim 8, wherein fatty acids of the soap are derived from a mixture of tallow and coconut oil.

11. The skin treatment composition according to claim 10, wherein 10 to 70% by weight of the fatty acids are derived from coconut oil and 90 to 30% by weight of the fatty acids are derived from tallow.

12. The skin treatment composition according to claim 1, comprising by weight about 10% disodium salt of monododecyl citrate, about 10% water and about 80% of a soap mixture comprised of from 75% to 85% of an alkali metal salt of fatty acids derived from tallow and from 15% to 25% of an alkali metal salt of fatty acids derived from coconut oil.

13. The skin treatment composition according to any preceding claim, including 30 to 70% by weight of a detergent active compound, 2 to 20% by weight of a suds booster, 10 to 40% by weight of an aliphatic fatty acid, 2.5 to 25% by weight of a water-soluble fatty acid soap, and 1 to 10% by weight of water.

14. A skin treatment composition according to claim 13 wherein the composition is formed into a toilet bar.

15. The skin treatment composition according to claim 13, wherein the detergent active compound is chosen from alkali metal, magnesium or ammonium salts of C_{12}-C_{16} hyroxyalkane sulfonates, C_8-C_{18} N-acyl taurinates, C_{12}-C_{18} alkyl sulfates, C_{12}-C_{18} alkyl ether sulfates, C_{12}-C_{16} alkyl phosphonates and phosphates, C_{12}-C_{16} mono-alkyl succinates and maleates, C_6-C_{14} dialkylsulfosuccinates, C_{15}-C_{20} alkane disulfonates C_8-C_{18} alkene sulfonates, alkylbenzene sulfonates and mixtures thereof.

16. The skin treatment composition according to claim 13, wherein the detergent active compounds are chosen from alkali metal, magnesium or ammonium salts of fatty acyl esters of isethionic acid.

17. The skin treatment composition according to claim 16, wherein the fatty acyl portion of the fatty acyl esters is derived from fatty acids having 10 to 18 carbon atoms.

18. The skin treatment composition according to claim 16, wherein the fatty acyl portion of the fatty acyl esters is derived from fatty acids derived from coconut oil.

19. The skin treatment composition according to any preceding claim, including 10 to 35% by weight of a soap or a detergent compound or a mixture of both, 1 to 5% by weight of a suds-boosting agent, 0.2 to 0.5% by weight of a preservative and the balance water.

20. The skin treatment composition according to any preceding claim, including 25 to 50% by weight stearic acid, 5 to 20% by weight coconut oil, 10 to 25% by weight glycerol, 1 to 15% by weight mineral

oil and 5 to 45% by weight water.

21. The skin treatment composition according to any preceding claim, wherein the physiologically acceptable carrier comprises an emollient.

22. The skin treatment composition according to claim 21, wherein the physiologically acceptable carrier comprises by weight 50 to 98% of an emollient and 1 to 15% of a thickening agent.

23. The skin treatment composition according to claim 22, wherein the salt of a monoester of citric acid and the emollient are mixed and formed into a solid stick.

24. The skin treatment composition according to claim 1 in ointment form including 1 to 5% by weight anhydrous wool fat, 5 to 20% by weight viscous paraffin, and 65 to 95% by weight white petroleum jelly.

25. The skin treatment composition according to claim 1 in cream form including 5 to 50% of an emollient and 50 to 95% by weight water.

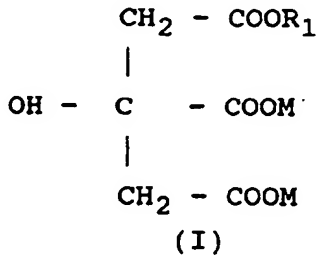
26. The skin treatment composition according to claim 1 in solution form including 65 to 99% by weight of an organic solvent suitable for solutions.

27. The skin treatment composition according to claim 1, wherein in the composition is incorporated in a closed metal container fitted with an aerosol cap and pressurized at from 172k Pascal (25 psi) up to 698k Pascal (100 psi) pressure with a propellant.

28. The composition according claim 1 in gel form including 5 to 64.5% by weight of an organic solvent suitable for gels, 0.5 to 5% by weight of a thickening agent, and the balance water.

Patentansprüche

1. Hautbehandlungszusammensetzung, umfassend 1 bis 35 Gew.-% eines Dikationsalzes eines Zitronensäuremonoesters oder einer Mischung von Zitronensäuremonoestern mit einer der folgenden Formeln:



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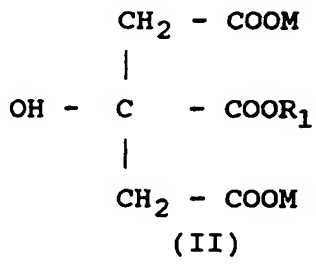


(II)

worin R_1 die Struktur eines Restes hat, der sich von R_1-OH ableitet, wobei der Alkohol ausgewählt ist aus Alkanolen, Alkenolen und Arylalkanolen mit 10 bis 18 Kohlenstoffatomen;
jedes M ein Kation ist, das unabhängig ausgewählt ist aus Alkalimetallen, Erdalkalimetallen, Ammonium-, Mono-, Di- und Trialkanolammoniumresten
und einen physiologisch annehmbaren Träger für den Monoester.

2. Hautbehandlungszusammensetzung nach Anspruch 1, worin R_1-OH ausgewählt ist aus geradkettigen Alkanolen und Alkenolen mit 10 bis 18 Kohlenstoffatomen.

3. Hautbehandlungszusammensetsung nach Anspruch 1 oder 2, worin R_1-OH ausgewählt ist aus Alkanolen und Alkenolen mit 12 bis 15 Kohlenstoffatomen.

4. Hautbehandlungszusammensetzung nach Anspruch 1, 2 oder 3, worin R_1-OH Laurylalkohol ist.

5. Hautbehandlungszusammensetzung nach einem der vorhergehenden Ansprüche, worin der Zitronensäuremonoester symmetrische und unsymmetrische Isomere in einem relativen Verhältnis von etwa 3:1 umfaßt.

6. Hautbehandlungszusammensetzung nach einem der vorhergehenden Ansprüche, umfassend 5 bis 30 Gew.-% eines Salzes eines Zitronensäuremonoesters oder einer Mischung von Zitronensäuremonoestern der Formeln (I) oder (II), 25 bis 90 Gew.-% Seife und als Ausgleich Wasser.

7. Hautbehandlungszusammensetzung nach Anspruch 6, worin die Fettsäuren der Seife aus Talg stammen.

8. Hautbehandlungszusammensetzung nach Anspruch 6, worin die Fettsäuren der Seife aus einem Pflanzenöl stammen.

9. Hautbehandlungszusammensetzung nach Anspruch 8, worin das Pflanzenöl Kokosnußöl ist.

10. Hautbehandlungszusammensetzung nach Anspruch 8, worin die Fettsäuren der Seife aus einer Mischung von Talg und Kokosnußöl stammen.

11. Hautbehandlungszusammensetzung nach Anspruch 10, worin 10 bis 70 Gew.-% der Fettsäuren aus Kokosnußöl stammen und 90 bis 30 Gew.-% der Fettsäuren aus Talg stammen.

12. Hautbehandlungszusammensetzung nach Anspruch 1, umfassend bezogen auf Gewicht etwa 10 % Dinatriumsalz von Monododecylcitrat, etwa 10 % Wasser und etwa 80 % einer Seifenmischung, die 75 bis 85 % Alkalisalze von Fettsäuren, die aus Talg stammen und 15 bis 25 % Alkalisalze von Fettsäuren, die aus Kokosnußöl stammen, umfaßt.

13. Hautbehandlungszusammensetzung nach einem der vorhergehenden Ansprüche einschließend 30 bis 70 Gew.-% einer aktiven Detergensverbindung, 2 bis 20 Gew.-% eines schaumfördernden Mittels, 10 bis 40 Gew.-% einer aliphatischen Fettsäure, 2,5 bis 25 Gew.-% einer wasserlöslichen Fettsäureseife und 1 bis 10 Gew.-% Wasser.

14. Hautbehandlungszusammensetzung nach Anspruch 13, worin die Zusammensetzung zu einem Seifenstück geformt ist.

15. Hautbehandlungszusammensetzung nach Anspruch 13, worin die aktive Detergensverbindung ausgewählt ist aus Alkali-, Magnesium- oder Ammoniumsalzen von C_{12}-C_{16}-Hydroxyalkansulfonaten, C_8-C_{18}-N-Acyltaurinaten, C_{12}-C_{18}-Alkylsulfaten, C_{12}-C_{18}-Alkylethersulfaten, C_{12}-C_{16}-Alkylphosphonaten und -phosphaten, C_{12}-C_{16}-Monoalkylsuccinaten und -maleaten, C_6-C_{14}-Dialkylsulfosuccinaten, C_{16}-C_{20}-Alkandisulfonaten, C_8-C_{18}-Alkensulfonaten, Alkylbenzolsulfonaten und Mischungen davon.

16. Hautbehandlungszusammensetzung nach Anspruch 13, worin die aktiven Detergensverbindungen ausgewählt sind aus Alkali-, Magnesium- oder Ammoniumsalzen von Fettacylestern der Isethionsäure.

17. Hautbehandlungszusammensetzung nach Anspruch 16, worin der Fettacylanteil des Fettacylesters aus Fettsäuren mit 10 bis 18 Kohlenstoffatomen stammt.

18. Hautbehandlungszusammensetzung nach Anspruch 16, worin der Fettacylanteil des Fettacylesters aus Fettsäuren stammt, die von Kokosnußöl abgeleitet sind.

19. Hautbehandlungszusammensetzung nach einem der vorhergehenden Ansprüche, einschließend 10 bis 35 Gew.-% einer Seife oder einer Detergensverbindung oder einer Mischung von beiden, 1 bis 5 Gew.-% eines schaumfördernden Mittels, 0,2 bis 0,5 Gew.-% eines Konservierungsmittels und als Ausgleich Wasser.

20. Hautbehandlungszusammensetzung nach einem der vorhergehenden Ansprüche, einschließend 25 bis 50 Gew.-% Stearinsäure, 5 bis 20 Gew.-% Kokosnußöl, 10 bis 25 Gew.-% Glycerin, 1 bis 15 Gew.-% Mineralöl und 5 bis 45 Gew.-% Wasser.

21. Hautbehandlungszusammensetzung nach einem der vorhergehenden Ansprüche, worin der physiologisch annehmbare Träger einen Weichmacher umfaßt.

22. Hautbehandlungszusammensetzung nach Anspruch 21, worin der physiologisch annehmbare Träger bezogen auf Gewicht 50 bis 98 % eines Weichmachers und 1 bis 15 % eines Verdickungsmittels umfaßt.

23. Hautbehandlungszusammensetzung nach Anspruch 22, worin das Salz eines Zitronensäuremonoesters und der Weichmacher vermischt werden und zu einem festen Stift geformt werden.

24. Hautbehandlungszusammensetzung nach Anspruch 1 in Form einer Salbe, die 1 bis 5 Gew.-% wasserfreies Wollfett, 5 bis 20 Gew.-% viskoses Paraffin und 65 bis 95 Gew.-% Vaseline einschließt.

25. Hautbehandlungszusammensetzung nach Anspruch 1 in Form einer Creme, die 5 bis 50 % eines Weichmachers und 50 bis 95 Gew.-% Wasser einschließt.

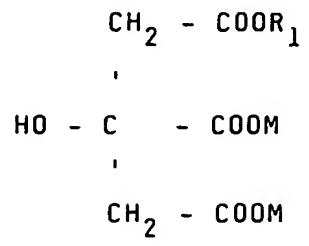
26. Hautbehandlungszusammensetzung nach Anspruch 1 in Form einer Lösung, die 65 bis 99 Gew.-% eines organischen Lösungsmittels, das für Lösungen geeignet ist, einschließt.

27. Hautbehandlungszusammensetzung nach Anspruch 1, worin die Zusammensetzung in einen geschlossenen Metallbehälter gebracht wird, der mit einem Aerosolverschluß versehen ist und mit einem Treibmittel auf einen Druck von 172 kPa (25 psi) bis 698 kPa (100 psi) gebracht wird.

28. Zusammensetzung nach Anspruch 1 in Form eines Gels, das 5 bis 64,5 Gew.-% eines organischen Lösungsmittels, das für Gele geeignet ist, 0,5 bis 5 Gew.-% eines Verdickungsmittels und als Ausgleich Wasser einschließt.

Revendications

1. Composition de traitement de la peau qui comprend :
de 1 à 35% en poids d'un sel dicationique d'un ou d'un mélange de monoester(s) d'acide citrique répondant à l'une des formules suivantes :



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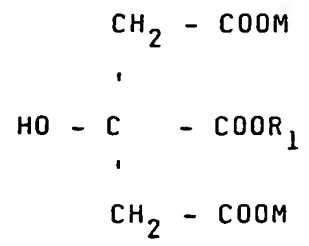

(II)

dans laquelle R_1 présente la structure d'un fragment dérivé de R_1-OH, alcool qui est choisi parmi les alcanols, les alcénols et les arylalcanols de 10 à 18 atomes de carbone ;
chaque M représente un cation indépendamment choisi parmi les métaux alcalins, les métaux alcalino-terreux, l'ammonium, les mono-, di- et tri-alcanol-ammoniums ; et
un véhicule physiologiquement acceptable pour ledit monoester.

2. Composition de traitement de la peau selon la revendication 1, dans laquelle R_1-OH est choisi parmi les alcanols et les alcénols à chaîne hydrocarbonée droite contenant de 10 à 18 atomes de carbone.

3. Composition de traitement de la peau selon la revendication 1 ou 2, dans laquelle R_1-OH est choisi parmi les alcanols et les alcénols de 12 à 15 atomes de carbone.

4. Composition de traitement de la peau selon la revendication 1, 2 ou 3, dans laquelle R_1-OH est l'alcool laurylique.

5. Composition de traitement de la peau selon l'une quelconque des revendications précédentes, dans laquelle le monoester d'acide citrique est constitué d'isomères symétriques et non symétriques dans un rapport relatif d'environ 3:1.

6. Composition de traitement de la peau selon l'une quelconque des revendications précédentes, comprenant de 5 à 30% en poids d'un sel d'un monoester ou d'un mélange de monoesters d'acide citrique de formule I ou II, de 25 à 90% en poids de savon, le complément étant de l'eau.

7. Composition de traitement de la peau selon la revendication 6, dans laquelle les acides gras du savon proviennent du suif.

8. Composition de traitement de la peau selon la revendication 6, dans laquelle les acides gras du savon proviennent d'une huile végétale.

9. Composition de traitement de la peau selon la revendication 8, dans laquelle l'huile végétale est l'huile de coco.

10. Composition de traitement de la peau selon la revendication 8, dans laquelle les acides gras du savon proviennent d'un mélange de suif et d'huile de coco.

11. Composition de traitement de la peau selon la revendication 10, dans laquelle de 10 à 70% en poids des acides gras proviennent d'huile de coco et de 90 à 30% en poids des acides gras proviennent du suif.

12. Composition de traitement de la peau selon la revendication 1, qui comprend, en poids, environ 10% de sel disodique de monododécylcitrate, environ 10% d'eau et environ 80% d'un mélange de savons constitué de 75 à 85% d'un sel de métal alcalin d'acides gras provenant du suif et de 15 à 25% d'un sel de métal alcalin d'acides gras provenant de l'huile de coco.

13. Composition de traitement de la peau selon l'une quelconque des revendications précédentes, comprenant de 30 à 70% en poids d'un composé détergent actif, de 2 à 20% en poids d'un agent de moussage, de 10 à 40% en poids d'un acide gras aliphatique, de 2,5 à 25% en poids d'un savon d'acide gras hydrosoluble et de 1 à 10% en poids d'eau.

14. Composition de traitement de la peau selon la revendication 13, dans laquelle la composition est façonnée en un pain de toilette.

15. Composition de traitement de la peau selon la revendication 13, dans laquelle le composé détergent actif est choisi parmi les sels de métaux alcalins, de magnésium ou d'ammonium, d'hydroxyalcanesulfonates en C_{12-16}, N-acyltaurinates en C_{8-18}, alkylsulfates en C_{12-18}, alkyléthersulfates en C_{12-18}, alkylphosphonates et phosphates en C_{12-16}, monoalkylsuccinates et maléates en C_{12-16}, dialkylsulfosuccinates en C_{6-14}, alcanedisulfonates en C_{16-20}, alcènesulfonates en C_{8-18}, alkylbenzènesulfonates et leurs mélanges.

16. Composition de traitement de la peau selon la revendication 13, dans laquelle les composés détergents actifs sont choisis parmi les sels de métaux alcalins, magnésium ou ammonium des esters acyliques gras de l'acide iséthionique.

17. Composition de traitement de la peau selon la revendication 16, dans laquelle la portion acyle gras des esters acyliques gras provient des acides gras de 10 à 18 atomes de carbone.

18. Composition de traitement de la peau selon la revendication 16, dans laquelle la portion acyle gras des esters acyliques gras provient des acides gras d'huile de coco.

19. Composition de traitement de la peau selon l'une quelconque des revendications précédentes, comprenant de 10 à 35% en poids d'un savon ou composé détergent ou un mélange des deux, de 1 à 5% en poids d'un agent de moussage, de 0,2 à 0,5% en poids d'un conservateur, le complément étant de l'eau.

20. Composition de traitement de la peau selon l'une quelconque ds revendications précédentes, comprenant de 25 à 50% en poids d'acide stéarique, de 5 à 20% en poids d'huile de coco de 10 à 25% en poids de glycérol, de 1 à 15% en poids d'une huile minérale et de 5 à 45% en poids d'eau.

21. Composition de traitement de la peau selon l'une quelconque des revendications précédentes, dans laquelle le véhicule physiologiquement acceptable comprend un émollient.

22. Composition de traitement de la peau selon la revendication 21, dans laquelle le véhicule physiologiquement acceptable comprend de 50 à 98% en poids d'un émollient et de 1 à 15% d'un épaississant.

23. Composition de traitement de la peau selon la revendication 22, dans laquelle on mélange et on forme en un bâtonnet solide le sel d'un monoester d'acide citrique et l'émollient.

24. Composition de traitement de la peau selon la revendication 1, sous forme d'un onguent comportant de 1 à 5% en poids de graisse de laine anhydre, de 5 à 20% en poids de paraffine visqueuse et de 65 à 95% en poids de gelée blanche de pétrole.

25. Composition de traitement de la peau selon la revendication 1, sous forme de crème comprenant de 5 à 50% d'un émollient et de 50 à 95% en poids d'eau.

26. Composition de traitement de la peau selon la revendication 1, sous forme d'une solution comprenant de 65 à 99% en poids d'un solvant organique approprié pour des solutions.

27. Composition de traitement de la peau selon la revendication 1, dans laquelle on incorpore la composition au sein d'un récipient métallique fermé muni d'un couvercle d'aérosol et pressurisé avec un propulseur à une pression comprise entre 172 kPa (25 psi) et 698 kPa (100 psi).

28. Composition selon la revendication 1, sous forme d'un gel comprenant de 5 à 64,5% en poids d'un solvant organique convenant pour des gels, de 0,5 à 5% en poids d'un épaississant, le complément étant de l'eau.